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(54) **EPOXY-AMINE COMPOSITIONS EMPLOYING UNSATURATED IMIDES.**

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Description

Field of the Invention

5 This invention relates to adhesive compositions exhibiting excellent adhesion to plastic substrates. More specifically, the compositions exhibit excellent adhesion to engineering plastics such as Valox™ (terphthalate polyesters, such as polybutylene terephthalate) and Ryton™ (polyphenylene sulfide). Even more specifically, the inventive compositions produce an adhesive bond that is resistant to the stress of thermal cycling and thermal shock. A significant use of these plastics, and thus for the adhesives, is in the construction of
10 electrical/electronic components.

Background of the Invention

The use of polyoxyalkylene amines as epoxy curatives is well known and is described, for example in
15 U.S. 4,485,229. In U.S. 4,051,195 and EP-A-0 245 559, there are also described formulations of epoxy and polyoxyalkylene amine and which utilize Michael addition of the amine to the acrylic component to provide crosslinking between the epoxy and acrylic components.

It is also known to use polyimides or various functionalized imide compounds, eg., aminoimide compounds, in epoxy formulations, see eg., U.S. 3,985,928, 3,763,087, and 4,092,442.

20 In U.S. 3,988,299 there are described anaerobic acrylic adhesives which display improved high temperature strength as a result of inclusion of a maleimide or nadimide compound.

In U.S. 4,490,515 there are described cyanoacrylate adhesives with maleimide or nadimide additives having improved strength at elevated temperatures.

While the use of maleimide or nadimide functional compounds as additives to improve hot strength
25 various curable adhesive or related systems has been previously described, applicants are unaware of any prior art suggesting that such additives can result in improved adhesion or thermal cycle resistance (i.e. resistance to loss of adhesion as a result of repeated large temperature changes.)

A major feature of the new engineering plastics that have been used for electronic applications is their thermal and dimensional stability. Thermal coefficients of expansion $<30 \times 10^{-5} \text{ K}^{-1}$ ($<30 \times 10^{-5}$ inch/inch deg c) are common. Usually the electrical/electronic component is of composite structure containing plastic,
30 ceramic and metal components. This situation is typified by potentiometers. Adhesive/Potting Compounds are used to encapsulate and protect electrical components from adverse environmental effects such as solvents or moisture. The adhesive component must retain its adhesion throughout the range of service conditions. One of the most severe tests the adhesive must withstand is delamination induced because of
35 the difference TCE's of the construction materials of electrical/electronic component.

Adhesive systems most commonly used to pot/encapsulate and bond electrical/electronic components are one and two-part epoxy resins. The resins are filled to a high level with mineral fillers, e.g., aluminum trihydrate to reduce shrinkage and TCE. However, these resins do suffer from significant process disadvantages such as slow cure. Moreover, their initial adhesion and thermal cycling properties are still not
40 always entirely satisfactory.

Traditional UV curable acrylic compositions are unsuitable due to high shrinkage on polymerization 8-15% and high TCE (of the order of $90 \times 10^{-5} \text{ K}^{-1}$ (90×10^{-5} inch/inch deg C)).

EP-A-0 245 559 and EP-A-0 313 574, describe compositions which exhibit advantages over both epoxies and UV curable acrylics. However, even these new materials can sometimes prove unsuitable for
45 bonding electrical/electronic components of composite structure where extreme thermal cycling and thermal shock is application requirement, i.e., -50 °C to 165 °C.

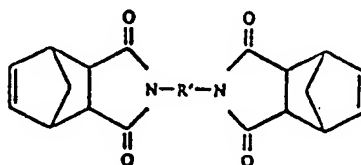
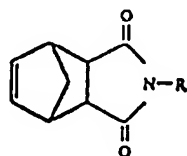
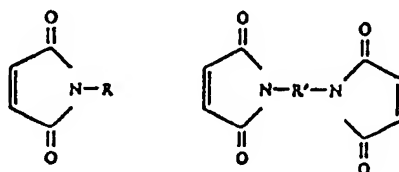
Summary of the Invention

50 The inventors have unexpectedly discovered that addition of mono or bis-unsaturated imide compounds to conventional epoxy/amine formulations in which the amine is a polyoxyalkylene polyamine results in significantly improved initial adhesion and thermal shock resistance over similar compositions without maleimide. The key to the thermal cycle resistance appears to be a surprising reduction in modulus of the cured product caused by amine-imide interaction when the polyoxyalkylene polyamine is used. Use of an
55 aromatic amine or an anhydride curing agent with an epoxy and imide formulation does not produce the improved initial adhesion or thermal shock resistance nor does use of imide compounds without unsaturation.

The present invention comprises a amine cured epoxy formulation which displays improved initial and thermal cycle strengths when bonding different materials such as Valox™ and aluminum.

The composition comprises:

- 1) a compound or mixture of compounds having a plurality of epoxy groups per molecule;
- 2) a polyoxyalkylene amine curative for the epoxy; and
- 3) an imide compound selected from those having the formulas:



wherein R and R' are, respectively, monovalent and divalent organic groups having 200 or fewer carbon atoms.

A further aspect of the invention comprises a method of bonding different materials, particularly polyalkylene terephthalate, polyalkylene terephthalate/polycarbonate blends or polyphenylene sulfide and metals of having a high thermal coefficient of expansion such as aluminum or copper using a cureable composition as disclosed above to provide a bonded assembly with improved thermal cycle resistance. In particular the invention provides a method of bonding two substrates of different materials characterised in that it comprises applying the composition as defined above between the substrates and joining the substrates in fixtured relationship for sufficient time to permit the composition to cure.

As yet a further aspect of the invention, a composition as described above may be modified by inclusion therein of an ethylenically unsaturated photocurable monomer such as an acrylic monomer and a photoinitiator in amounts effective to permit the composition to be immobilized on irradiation. Such modified compositions retain the improved initial adhesion and thermal cycle properties of the inventive compositions and additionally permit the formulation to be rapidly immobilized so as to facilitate continuous automated assembly operations.

A still further aspect of the invention comprises electronic components potted in a housing of polybutylene terephthalate, polybutylene terephthalate, polycarbonate blend or polyphenylene sulfide wherein the potting material is one of the cured compositions described above.

Detailed Description of the Invention

The epoxy component of the inventive composition is a monomeric, oligomeric or polymeric compound having two or more epoxy groups per molecule. Mixtures of such compounds may also be utilized.

Suitable epoxy resins include those derived from epichlorohydrin and dihydric phenols, e.g., resorcinol, hydroquinone, bisphenol A, p-p'-dihydroxydiphenylethane, bis-(2-hydroxynaphthyl)ethane, and 1,5-dihydroxynaphthalene. The epoxy compound may also be a cycloaliphatic epoxy or an epoxidized novolak. Suitable

epoxy compounds are described in "Handbook of Epoxy Resins" by Lee and Neville, McGraw-Hill Book Co., New York (1967). A diglycidyl ether of bisphenol A (DGEBA) is preferred.

In lieu of the above-described epoxy functional polymerizable monomers, or alternatively in association therewith, various epoxidized rubbers may be utilized in the potting compositions of the invention as the second resin component, such materials being well known in the art.

A useful class of such epoxidized rubbers are epoxidized carboxy terminated butadiene acrylonitrile copolymers sold under the name of Kelpoxy by Spencer Kellogg, and epoxidized polybutadiene, for example Oxiron 2001 commercially available from FMC Corporation. Still other suitable rubber epoxy additives are the various polymers sold by B.F. Goodrich Company under the name HYCAR.

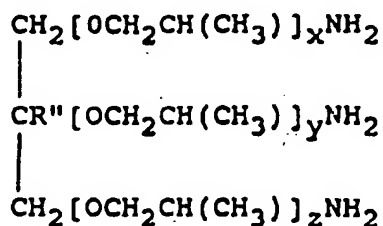
The amine component is limited to polyoxyalkylene amines having two or more aliphatic amino groups per molecule. The polyether backbone is based preferably either on propylene oxide or ethylene oxide or mixtures of the two. Such polyoxyalkylene amines are sold under the trademarks JEFFAMINE™ and TERATHANE™.

Preferably, the polyoxyalkylene polyamines have the structure



wherein Y is hydrogen, a methyl radical or an ethyl radical, Z is a hydrocarbon radical of 2-5 carbon atoms, n is at least one and r is a number greater than or equal to 2.

Especially preferred are polyoxyalkylene polyamines having the general structure:

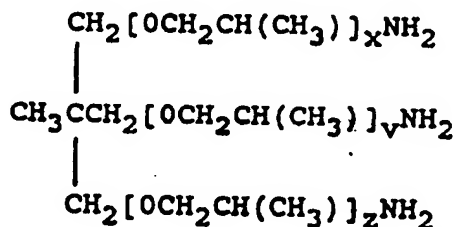


wherein $x+y+z$ are numbers having a total such that the molecular weight of said polyoxyalkylene polyamine is about 400 or more and R'' is H or alkyl.

Preferred low molecular weight polyoxyalkylene polyamines have the general structure:



wherein w is a finite number such that the molecular weight of said polyoxyalkylene polyamine is from about 200 to about 300, or of the general structure:

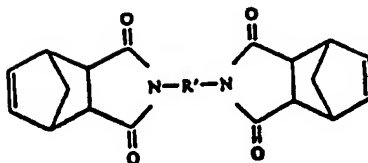
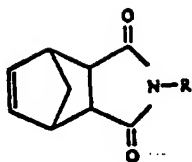
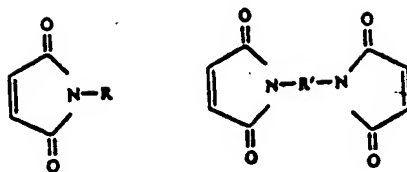


wherein $x+y+z$ are finite numbers having a total such that the molecular weight of said polyoxyalkylene polyamine is about 400.

Preferred high molecular weight polyoxyalkylene polyamines are structures with more than two branches having a molecular weight of 5000 or more.

The amine hardener is used in a stoichiometric equivalent to the epoxy resin.

Suitable olefinic imide adhesion promoters include maleimides and norbornene functionalized imides. Such imides are represented by the formulas:



wherein R and R' are respectively monovalent and divalent organic groups. R and R' may be aliphatic or divalent organic groups aromatic heterocyclic radicals optionally substituted with alkoxy, cyano or other organic groups, or groups consisting of several said radicals. Further R & R' may include non-carbon substituents such as halogens. The R or R' group suitably contains less than 200 carbon atoms, more suitably less than 50 carbon atoms. Generally it is preferred that the imide compound be a bismaleimide and that R' be a C₂ - C₂₀ hydrocarbon group.

Certain of the preferred dimaleimides are shown in the working examples. In addition, specific attention is directed to compounds such as N,N'-ethylenedimaleimide, N,N'-hexamethylenedimaleimide, N,N'-decamethylenedimaleimide, N,N'-dodecamethylenedimaleimide, N,N'-oxydipropylenedimaleimide, ethylenedioxy bis(N-propylmaleimide), N,N'-metaphenylenedimaleimide, N,N'-paraphenylenedimaleimide, N,N'-oxy(diparaphenylene) dimaleimide, N,N'-methylene (diaparaphenylene)dimaleimide, N,N'-ethylene-(diparaphenylene)dimaleimide, N,N'-sulfo(diparaphenylene)- dimaleimide, N,N'-metaphenylene-bis-(paraoxyphenylene)dimaleimide, N,N'-methylene(di-1,4-cyclohexylene)-dimaleimide, N,N'-isopropylidene(di-1,4-cyclohexene)dimaleimide, 2,5-oxadiazolylenedimaleimide, N,N'-paraphenylene(dimethylene) dimaleimide, N,N'-2-methylparatolulene dimaleimide, N,N'-hexamethylenedicitraconimide, N,N'-thio(diphenylene)-dicitraconimide, N,N'-methylene(diparaphenylene)-bis(chloromaleimide) and N,N'-hexamethylene-bis-(cyanomethylmaleimide).

Preferred bismaleimides include 4,4'-bismaleimidodiphenylmethane (from Ciba Geigy), 1,4 pyrrole-2,5-dione-1,1-(methylenedi-1,4-phenylene) bis-polymer with methylene bis(benzamine) (Keramide® 1050 from Rhone Poulenc), and 1,1-(methylenedi-4,1-phenylene)bismaleimide (from Reichold Chemicals).

Norbornene functionalized imides are described, in U.S. Patent Ser. No. 4 808 638 filed September 21, 1987.

The imide component is generally used at a level of 0.1 to 10% with 1 to 5 percent being the preferred levels.

As a further embodiment of the invention the formulation may include a photocurable ethylenically unsaturated compound and a photoinitiator in an amount effective to cause the composition to become immobilized upon irradiation with actinic light.

Suitable unsaturated compounds include (meth)acrylate compounds, vinyl monomers and unsaturated polyesters solubilized in vinyl resins. (Meth)acrylic esters are preferred.

As used here in the term "(meth)acrylic" is intended to be broadly construed to include acrylic as well as methacrylic compounds, e.g., acrylic esters and methacrylic esters.

Useful acrylic resins include esters and amides of (meth)acrylic acid as well as co-monomers thereof with other co-polymerizable monomers. Illustrative esters include methyl acrylate, methyl methacrylate, hydroxy ethyl acrylate, butyl methacrylate, octyl acrylate, and 2-ethoxyethyl acrylate. Illustrative amides

include butoxymethyl acrylamide, methacrylamide, and tert-butyl acrylamide. Also suitable are copolymers of such compounds, and copolymers with other monomers containing polymerizable vinyl groups. Polyacrylates are generally useful, including 1,3-butylene glycol diacrylate, diethylene glycol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate, pentaerythritol tetraacrylate, tripropylene glycol diacrylate, ethoxylated bisphenol-A-diacrylate, trimethylolpropane dipentaerythritol pentaacrylate, pentaerythritol triacrylate, and the corresponding methacrylate compounds. Also useful are reaction products of (meth)acrylic acid and epoxide resins and urethane acrylic resins. Suitable poly (meth)acrylate ester compounds are also described in U.S.-A-4,051,195; US-A-2,895,950; US-A-3,218,305; and US-A-3,425,988.

It will be understood that the foregoing listing of (meth)acrylic compounds is intended only to be illustrative in character, and that any other resin compounds having (meth)acrylic functionality in their molecules and curable under actinic radiation conditions may be potentially employed.

Among the foregoing compounds, (meth)acrylic acid esters are preferred, with the most preferred compounds being (meth)acrylic acid esters of polyhydric alcohols, such as ethoxylated trimethylolpropane triacrylate and dipentaerythritol monohydroxy pentaacrylate.

Another class of resins which are actinic radiation curable and suitable for use in the compositions in the invention include vinyl monomers such as styrene, vinyl toluene, vinyl pyrrolidone, vinyl acetate, divinyl benzene, and the like.

A further class of actinic radiation curable materials comprises unsaturated polyesters, solubilized in vinyl monomers, as ordinarily prepared from alpha-beta ethylenically unsaturated polycarboxylic acids and polyhydric alcohols. Such polyesters are described for example in U.S.-A-4,025,407.

As used herein, "actinic radiation" means electromagnetic radiation having a wavelength of about 700 nm or less which is capable, directly or indirectly, of curing the specified resin component of the potting composition. By indirect curing in this context is meant curing under such electromagnetic radiation conditions as initiated, promoted or otherwise mediated by another compound.

Suitable photoinitiators useful with ultraviolet (UV) actinic radiation curing of (meth)acrylic and vinyl monomers include free radical generating UV initiators such as benzophenone, diethoxy-acetophenone, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, diethoxyxanthone, chlorothioxanthone, azo-bis-isobutyronitrile, N-methyl diethanolaminebenzophenone, and mixtures thereof.

In addition, the combination of a hydroperoxide, such as cumene hydroperoxide, with a η^6, η^5 -arene complex as described in WO 88/02879 of Woods et al., filed October 14, 1986, is suitable and in fact preferred as the photoinitiator. Such combinations are useful with both UV and visible irradiation.

Visible light initiators include camphorquinone/peroxyester initiators and 9-fluorene carboxylic acid peroxyesters.

Infrared initiators also include cumene hydroperoxide benzoyl peroxide, azobisisobutyronitrile, and like azo and peroxide compounds.

The amount of the photoinitiator required for a given composition may be readily determined by the expedient of simple experiment, without undue effort. In general, however, in the case of (meth)acrylic and vinyl first resin components, amounts of photoinitiator on the order of about 0.1-10 percent by weight, and preferably about 0.5-5 percent by weight, based on the weight of the total resin, have been found satisfactory.

The amount of the unsaturated component may constitute 50% of the weight of the total composition. Preferably the level of the first resin component is between 0.1 and 20% based on the weight of the total composition, and more preferably between 5 and 15%.

It is particularly surprising that the advantages of the invention are still obtained when (meth)acrylic or other vinyl resins capable of Michael addition to the amine component are employed in the inventive epoxy compositions. The competing reactions for amine between epoxy and imide are further complicated by the addition of the reactive acrylic or similar groups. While an increase in thermal decomposition resistance might be expected, it would also be expected that addition of the imide would cause an increase in the rigidity of the cured formulation with a consequent decrease in thermal shock resistance. Use of an acrylic resin would be expected to make this problem worse. Instead, addition of the imide dramatically decreases the modulus and increases elongation at break. Apparently the imide reduces rather than increases the crosslink density of the cured product.

The advantages of the invention are further illustrated with respect to the following non-limiting examples, wherein all parts and percentages are by weight unless otherwise expressly stated and all references to Valox™ pertain to Valox™ 420 SEO, a filled polybutylene terephthalate containing a minor amount of polycarbonate.

EXAMPLE 1

This example illustrates the advantages of the invention over comparable compositions which do not include the imide component.

5 The adhesive compositions of Table I were prepared and the respective parts mixed and applied to lap shear specimens (as per ASTM D1002). Cure of the compositions was effected at 121.1°C (250°F) for 15 minutes. Tensile shear strengths were obtained on samples aged at room temperature and on samples thermally shocked by subjecting them to 10 cycles of -55° to 125°C. The results are set forth in Table I.

10

Table I

COMPOSITION	1*	2
<u>Part A</u>		
Diglycidyl ether bisphenol A		
(Dow Quatrex 1010)	80.0	80.0
<u>Part B</u>		
Polyoxypropylenamine		
(Texaco Jeffamine D230)	25.0	20.0
Keramide 1050		
(Rhône Poulenc)	<u>0.0</u>	<u>5.0</u>
<u>Mix Ratio</u>		
(A/B)	80/25	80/25

35

Tensile Shear Strength kPa (psi)
ASTM D1002

40

<u>Substrate</u>	<u>Composition</u>	
	1*	2
Valox™ to Aluminum		
Room temp aged	5895.0 (855)	10245.6 (1486)
Thermal Shocked		
(10 cycles -55° to 125°C)	0 (0)	5502.0 (798)

50

* comparative example

55 EXAMPLE 2

In this example, the formulations in Table II were prepared and used as potting compositions for variable resistance type potentiometers. The potentiometer was a model 3006 Industrial Cermet Trimpot-

potentiometer commercially available from Bourns, Inc. (Riverside, CA), and had a housing of Valox polybutylene terephthalate.

Part A and B for compositions 3 and 4, Table II were mixed by extrusion through static mixing elements. Potentiometers were potted with both mixed compositions and the potting compositions cured under 5 seconds irradiation at 100,00 microwatts per square centimeter, 360 nanometers wavelength, followed by oven curing at 121.1 °C (250 °F) for 15 minutes.

Microscopic examination X30 of components potted with either composition revealed no evidence of delamination of the potting materials from the component housing.

Thermal shocking of the components was carried out, 10 cycles of -55 ° to 125 °C. Subsequently on reexamination of the components, delamination was evident in those components potted with composition 3, whereas no delamination was evident for components potted with composition 4.

This example illustrates how incorporation of the bismaleimide confers improved thermal cycle resistance to the potting composition. The improved thermal cycle resistance is believed to be due to the surprisingly lower modulus of composition 4.

Table II

COMPOSITION	<u>3</u> *	<u>4</u>
<u>Part A</u>		
Diglycidyl ether bisphenol A (Dow Quatrex 1010)	75.3	75.3
Dipentaerythritol monohydroxy pentaacrylate (Sartomer SSR399)	21.2	21.2

1 - benzoyl cyclohexanol	3.0	3.0
4.4'-Bismaleimidodiphenylmethane		
(Matrimide 5292, Ciba Geigy)	0.0	10.0
Organic Air Release Agent		
(Byk Asol Byk Malinkrodt)	<u>0.5</u>	<u>0.5</u>

10

Part B

Polyoxypropylenamine

(Texaco Jeffamine D230)	23.8	23.8
Aluminum Oxide	66.2	66.2
Silicon Dioxide	2.0	2.0
C14 Aliphatic Diacrylate		
(Sartomer Chemlink C2000)	<u>8.0</u>	<u>8.0</u>
<u>Mix Ratio</u>		
(A/B)	1/1	1.1/1

25

Mechanical and Electrical Properties

<u>COMPOSITION</u>	<u>3*</u>	<u>4</u>
Tensile Strength	2582	642
Modulus	205,07	1859
% Elongation at		
Break	9.4	38.4
Hardness Shore D	.83	47
Surface Resistivity (ohms)	6×10^{14}	1.9×10^{14}
Volume Resistivity (ohm-cm)	6×10^{14}	8.3×10^{13}

40

* comparative example

45 EXAMPLE 3

The adhesive compositions of Table III were prepared and respective Parts A and B mixed and applied to lap shear specimens (as per ASTM D1002). Adhesive lap shear bonds were prepared and cure of the compositions was effected by heat curing at 121.1°C (250°F) for 10 minutes. It can be seen from the results in Table III that Composition 6 of Table III offers improved thermal cycle resistance over Composition 5 of Table III, and that Composition 7 of Table III offers further improved thermal cycle resistance over Composition 5 and, in addition, improved adhesion on unaged samples over Composition 5 of Table III. This illustrates the improved thermal shock resistance resulting from the use of maleimides on differential substrate bonding. The improvement is more pronounced with a bismaleimid over the simple N-phenylmaleimide.

55

Compositions 6 and 7 thus offer advantages over Composition 5 in potting or bonding on differential substrates.

Table III

5	COMPOSITION	<u>5*</u>	<u>6</u>	<u>7</u>
	<u>Part A</u>			
	Diglycidyl ether bisphenol A			
	(Dow Quatrex 1010)	75.3	75.3	75.3
10	Dipentaerythritol monohydroxy			
	pentaacrylate (Sartomer SSR399)	21.2	21.2	21.2
	1 - benzoyl cyclohexanol	3.0	3.0	3.0
15	Keramide 1050			
	(Rhône Poulenc)	0.0	0.0	10.0
	N-phenyl maleimide (Imilex™-P)	0.0	10.0	0.0
20	Organic Air Release Agent			
	(Byk Asol Byk Malinkrodt)	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>
	<u>Part B</u>			
25	Polyoxypropyleneamine			
	(Texaco Jeffamine D230)	23.8	23.8	23.8
	Aluminum Oxide	66.2	66.2	66.2
	Silicon Dioxide	2.0	2.0	2.0
30	C14 Aliphatic Diacrylate			
	(Sartomer Chemlink C2000)	<u>8.0</u>	<u>8.0</u>	<u>8.0</u>

35

40

45

50

55

Mix Ratio

(A/B)

1/1 1.1/1 1.1/1

5

TABLE III (con't)

Tensile Shear Strengths kPa (psi)

10

ASTM D1002

Substrate

15

Composition5 * 6 7

Valox™ to Aluminum

Room temperature aged 4095.5 (594) 3592.2 (521) 5081.4 (737)

20

Thermal Shocked

10 cycles -55° to 125°C 0 (0) 792.9 (115) 3723.2 (540)

* comparative example

25

EXAMPLE 4

The adhesive compositions of Table IV were prepared and respective Parts A and B mixed, and the mixtures applied to lap shear specimens as per ASTM D1002. Adhesive lap shear bonds were prepared and cure of the compositions effected by heat curing at 121.1°C (250°F) for 15 minutes. It can be seen from the results in Table IV that Composition 9 of Table IV offers equivalent or better adhesive performance on all the substrates tested, and offers significantly improved thermal shock resistance over Composition 8. This example illustrates the effectiveness of imides with suitable terminal unsaturation other than mal-imides. Composition 10, however, offered no improvement and these results illustrate that a nonfunctional polyimide is not effective in the invention.

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Table IV

COMPOSITION		<u>8*</u>	<u>9</u>	<u>10*</u>
<u>Part A</u>				
5	Diglycidyl ether bisphenol A (Dow Quatrex 1010)	5.3	75.3	75.3
10	Dipentaerythritol monohydroxy pentaacrylate (Sartomer SSR399)	21.2	21.2	21.2
	1 - benzoyl cyclohexanol	3.0	3.0	3.0
15	Bis-methylnadimide of 1,3- phenylene diamine	0.0	10.0	0.0
	Nonfunctional imide (Matrimide 5218, Ciba Geigy)	0.0	0.0	10.0
20	Organic Air Release Agent (Dyk Asol Dyk Malinkrodt)	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>
<u>Part B</u>				
25	Polyoxypropylenamine (Texaco Jeffamine D230)	23.8	23.8	23.8
	Aluminum Oxide	66.2	66.2	66.2
	Silicon Dioxide	2.0	2.0	2.0
30	C14 Aliphatic Diacrylate (Sartomer Chemlink C2000)	<u>8.0</u>	<u>8.0</u>	<u>8.0</u>
<u>Mix Ratio</u>				
	(A/B)	1/1	1.1/1	1.1/1

Tensile Shear Strengths kPa (psi)

ASTM D1002

<u>Substrate</u>	<u>Composition</u>		
	<u>8*</u>	<u>9</u>	<u>10*</u>
45	Valox™ to Aluminum		
	Room temperature aged	4095.5 (594)	4329.9 (628) 1316.9 (191)
	Thermal Shocked		
50	10 cycles -55° - 125° C	0 (0)	1958.1 (284) 0 (0)

	Ryton™ to glass	176	189	296
	Ryton™ to aluminium	323	325	364
5	Valox™ to glass	771	846	681

* comparative example

10

EXAMPLE 5

15 The adhesive compositions of Table V were prepared, equal weights of respective Parts A and B mixed, and the mixtures were applied to lap shear specimens as per ASTM D1002. Cure of the compositions effected by heat curing at 121.1 °C (250 °F) for 10 minutes. It can be seen from the results in Table V that the use of the maleimide had no beneficial effect when used with an anhydride cured epoxy composition confirming the need for an amine hardner for the epoxy resin.

20

Table V

	COMPOSITION	<u>11*</u>	<u>12*</u>
25	<u>Part A</u>		
	Cryacure 6110 (Union Carbide)	29.4	29.9
	cycloaliphatic bis-epoxide		
30	Cryacure 6351 (Union Carbide)		
	cycloaliphatic bis-epoxide	43.7	46.3
	Dipentaerythritol monohydroxy		
35	pentaacrylate (Sartomer SSR399)	18.5	17.6
	Dietoxyacetophenone	2.0	2.8
	Keramide 1050 (Rhône Poulenc)	0.0	5.0
40	Organic Air Release Agent		
	(Byk Asol Byk Malinkrodt)	<u>0.5</u>	<u>0.5</u>

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Part B

ACDP-1 Anhydride blend

5	(Anhydrides and Chemicals)	80.0	76.0
	Dipentaerythritol monohydroxy-		
	pentaacrylate	20.0	19.0
10	Keramide 1050 (Rhone Poulenc)	<u>0.0</u>	<u>5.0</u>
	<u>Mix Ratio</u>		
	(A/B)	1/1	1/1

15 Tensile Shear Strength kPa (psi)
 ASTM D1002

20	<u>Substrate</u>	<u>Composition</u>	
		<u>11*</u>	<u>12*</u>
	Valox™ to glass	606.7 (88)	451.1 (66)
25	Valox™ to Aluminum		
	Room temp aged	517.1 (75)	937.7 (136)
	Thermally Shocked		
	10 cycles -55° to 125°C	0 (0)	0 (0)

30

* comparative example

35 EXAMPLE 6

The adhesive compositions of Table VI were prepared, mixed, applied to lap shear specimens and cured as in EXAMPLES 3-5. It can be seen from the results in Table VI that the substitution of an aromatic amine for the polyoxyalkylene amine produces a cured composition with no significant beneficial effect on thermal shock resistance.

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Table VI

COMPOSITION	<u>13*</u>	<u>14*</u>
<u>Part A</u>		
Diglycidyl ether bisphenol A (Dow Quatrex 1010)	75.3	75.3
Dipentaerythritol monohydroxy pentaacrylate (Sartomer SSR399)	21.2	21.2
1 - benzoyl cyclohexanol	3.0	3.0
Keramide 1050 (Rhone Poulenc)	10.0	10.0
Organic Air Release Agent (BYK Asol 501, Malinkrodt)	<u>0.5</u>	<u>0.5</u>
<u>Part B</u>		
Polyoxypropylenamine (Texaco Jeffamine D230)	23.8	0
Aromatic Amine (Ciba Geigy XUHY 350)	0	23.8
Aluminum Oxide	66.2	66.2
Silicon Dioxide	2.0	2.0
C14 Aliphatic Diacrylate (Sartomer Chemlink C2000)	<u>8.0</u>	<u>8.0</u>
<u>Mix Ratio</u> (A/B)	1.1/1	1.1/1

Tensile Shear Strength kPa (psi)

ASTM D1002

Substrate

Valox™ to Aluminum		
Room temp aged	5081.4 (737)	3681.8 (534)
Thermal Shocked 10 cycles -55° - 125° C	3732.2 (540)	572.3 (83)

* comparative example

EXAMPLE 7

On mixing equal parts of parts A and B below, a mixture is produced which, when applied to potentiometer assemblies (i.e. Mepco Electra) and cured according to the cure schedule below, gives a seal

which can withstand extensive thermal shock of -60°C to 150°C without showing any delamination from the Valox housing or any cracking within the sealant material.

Part A

Diglycidylether of Bisphenol A	34.78%
EPI-REX 5048 (aliphatic triglycidyl ether)	34.78
1-Benzoyl Cyclohexanol	1.83
BYK 052 wetting agent	0.18
dipentaerythritol monohydroxy pentaacrylate (Sartomer, SR399)	19.22
Pennco Black dispersion (Carbon black in TRPDGA* 20% w)	0.40
Keramide 1050 (Rhone-Poulenc)	9.15

Part B

Jeffamine D230 (polyoxypropylene diamine)	23.8
Sartomer SR2000 (C14 aliphatic diol diacrylate)	8.0
Silicon dioxide	1.0
Alumina	67.2

*tripropylene glycol diacrylate

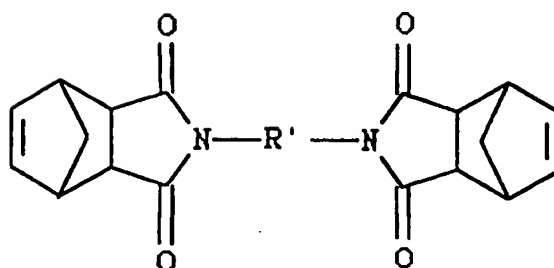
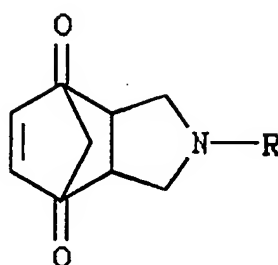
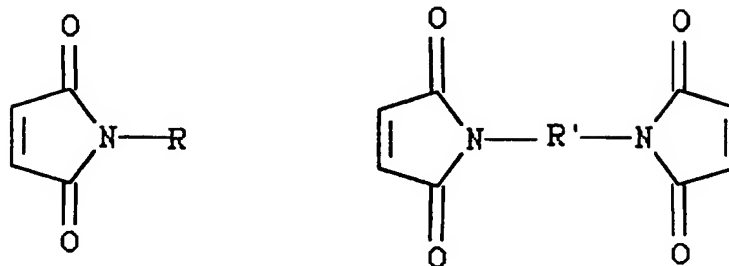
Cure Schedule:

Immobilization	10 sec UV 70,000 W cm ²
Cure	10 minutes 121.1°C (250°F)

Claims

1. A composition characterised in that it comprises:
 - 1) a compound or mixture of compounds having a plurality of epoxy groups per molecule;
 - 2) a polyoxyalkylene amine curative for the epoxy; and

3) an imide compound selected from those having the formulas:



wherein R and R' are, respectively, monovalent and divalent organic groups having 200 or fewer carbon atoms.

2. A composition as claimed in claim 1 characterized in that the epoxy component is a cycloaliphatic epoxy, an epoxidized novolac, an epoxidized rubber or a resin derived from epichlorohydrin and dihydric phenols.
3. A composition as claimed in claim 1 or 2 characterized in that the epoxy component is a diglycidyl ether of bisphenol A.
4. A composition as claimed in any of claims 1 to 3 characterized in that it comprises photocurable ethylenically unsaturated compound and a photoinitiator.
5. A composition as claimed in claim 4 characterized in that the ethylenically unsaturated compound is a (meth)acrylic ester.
6. A composition as claimed in any of claims 1 to 5 characterized in that the polyoxyalkylene amine is represented by the structure:



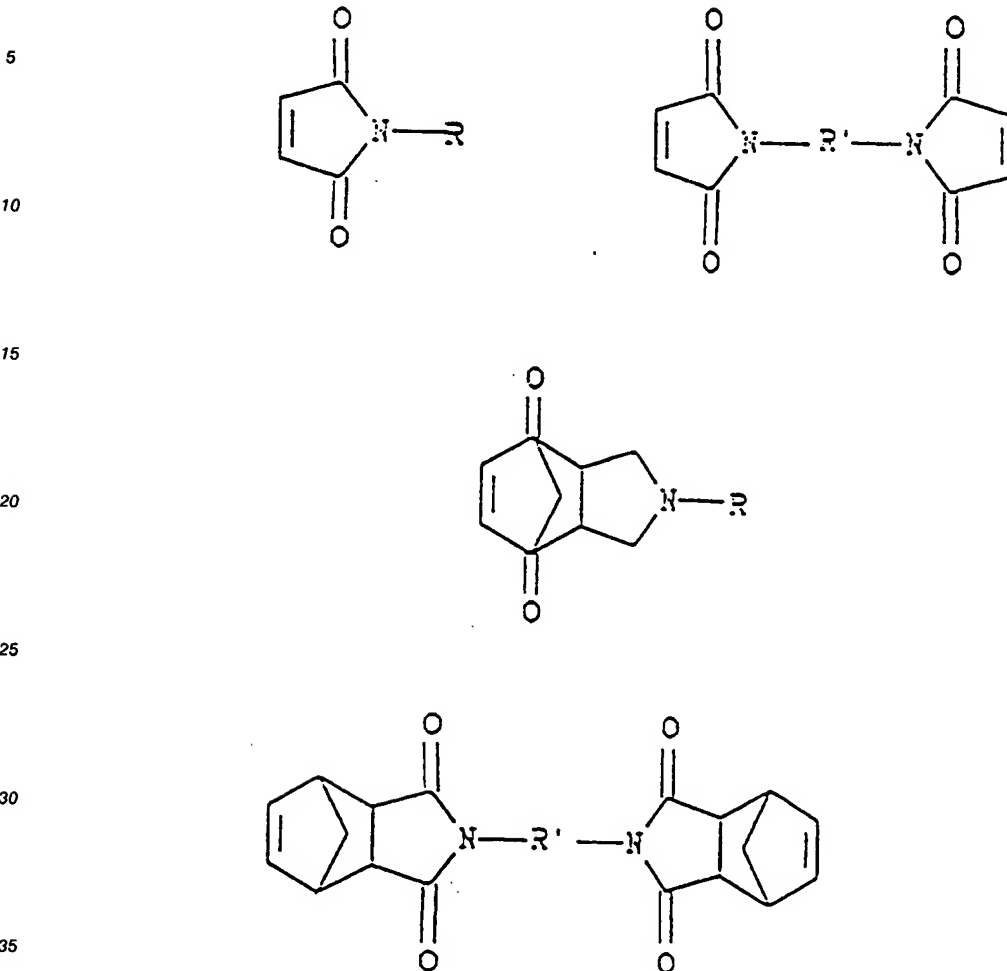
wherein Y is hydrogen, a methyl radical or an ethyl radical, Z is a hydrocarbon radical of 2-5 carbon atoms, n is at least one and r is a number greater than or equal to 2.

7. A composition as claimed in claim 6 characterized in that the r is greater than 2 and the molecular weight of the polyoxyalkylene amine is 5,000 or more.
8. A composition as claimed in any of claims 1 to 7 characterized in that the imide is N,N'-ethylenedimaleimide, N,N'-hexamethylenedimaleimide, N,N'-decamethylenedimaleimide, N,N'-dodecamethylenedimaleimide, N,N'-oxydipropylenedimaleimide, ethylenedioxy bis(N-propylmaleimide), N,N'-metaphenylenedimaleimide, N,N'-paraphenylenedimaleimide, N,N'-oxy(diparaphenylene) dimaleimide, N,N'-methylene-(diparaphenylene)dimaleimide, N,N'-ethylene-(diparaphenylene)dimaleimide, N,N'-sulfo(diparaphenylene)- dimaleimide, N,N'-metaphenylene-bis(paraoxyphenylene)dimaleimide, N,N'-methylene(di-1,4-cyclohexylene)-dimaleimide, N,N'-isopropylidene(di-1,4-cyclohexylene)dimaleimide, 2,5-oxadiazolylenedimaleimide, N,N'-paraphenylene(dimethylene) dimaleimide N,N'-2-methyl-paratoluylene dimaleimide, N,N'-hexamethylenedicitraconimide, N,N'-thio(diphenylene)dicitraconimide, N,N'-methylene-(diparaphenylene)-bis(chloromaleimide) or N,N'-hexamethylene-bis(cyanomethylmaleimide).
9. A composition as claimed in claim 8 characterized in that the imide is 4,4'-bismaleimidodiphenylmethane, 1,4 pyrrole-2,5-dione-1,1-(methylenedi-1,4-phenylene) bis-polymer with methylene bis-(benzamine) and 1,1-(methylenedi-4,1-phenylene)bismaleimide.
10. A composition as claimed in any of claims 1 to 9 wherein the imide component is present in the range of 0.1-10%.
11. A composition as claimed in claim 10 characterized in that the imide component is present in the range of 1-5%.
12. A method of bonding two substrates of different materials characterized in that it comprises applying a composition as claimed in claim 1 between the substrates and joining the substrates in fixtured relationship for sufficient time to permit the composition to cure.
13. A method as claimed in claim 12 characterized in that the first substrate is a polyalkylene terephthalate, polyalkylene terephthalate/polycarbonate blend or polyphenylene sulfide and the second substrate is a metal having a high thermal coefficient of expansion.
14. A method as claimed in claim 13 characterized in that the second substrate is aluminum or copper.
15. An electronic component potted in a housing of polybutylene terephthalate, polybutylene terephthalate, polycarbonate blend or polyphenylene sulfide wherein the potting material is a cured composition as claimed in claim 1.

Patentansprüche

1. Eine Zusammensetzung, die dadurch gekennzeichnet ist, daß sie
 - 1) eine Verbindung oder eine Mischung von Verbindungen, die eine Mehrzahl von Epoxygruppen pro Molekül enthalten,
 - 2) ein Polyoxyalkylenamin-Vernetzungsmittel für Epoxy, und

3) eine Imidverbindung, ausgewählt aus solchen mit den nachstehenden Formeln



in denen R und R' monovalente bzw. divalente organische Gruppen mit 200 oder weniger Kohlenstoffatomen bedeuten, enthält.

- 40
2. Eine Zusammensetzung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Epoxykomponente ein cykloaliphatisches Epoxy, ein epoxydierter Novolak, ein epoxydirtes Gummi oder ein Harz, abgeleitet von Epichlorhydrin und einem zweiwertigen Phenol, ist.
- 45
3. Eine Zusammensetzung gemäß den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die Epoxykomponente ein Diglycidylether von Bisphenol A ist.
4. Eine Zusammensetzung gemäß den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß sie eine photovernetzbare ethylengruppenhaltige ungesättigte Verbindung und einen Photoinitiator enthält.
- 50
5. Eine Zusammensetzung gemäß Anspruch 4, dadurch gekennzeichnet, daß die ethylengruppenhaltige ungesättigte Verbindung ein (Meth)acrylsäureester ist.
- 55
6. Eine Zusammensetzung gemäß jedem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Polyoxyalkylenamin durch die Strukturformel



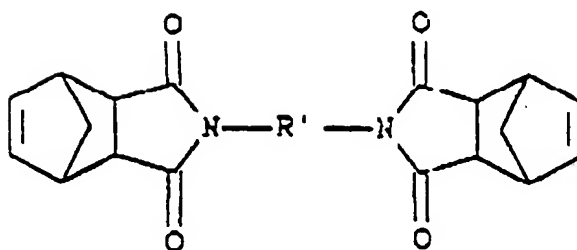
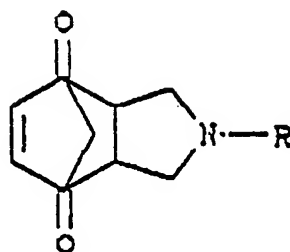
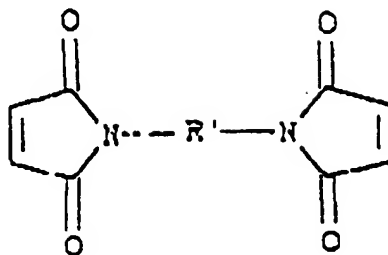
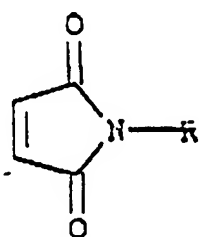
dargestellt wird, in der Y Wasserstoff, eine Methylgruppe oder eine Ethylgruppe, Z eine Kohlenwasserstoffgruppe mit 2 - 5 Kohlenstoffatomen, n zumindest 1 und r eine Zahl, die größer od r gleich 2 ist, bedeuten.

- 5 7. Eine Zusammensetzung gemäß Anspruch 6, dadurch gekennzeichnet, daß r größer als 2 ist und das Molekulargewicht des Polyoxyalkylenamins 5.000 oder mehr beträgt.
8. Eine Zusammensetzung gemäß jedem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß das Imid N,N'-Ethylen-dimaleinimid, N,N'-Hexamethylen-dimaleinimid, N,N'-Decamethylen-dimaleinimid, N,N'-Dodecamethylen-dimaleinimid,
10 N,N'-Oxydipropylen-dimaleinimid, Ethylendioxy-bis-(N-propylmaleinimid), N,N'-m-Phenylen-dimaleinimid, N,N'-p-Phenylen-dimaleinimid, N,N'-Oxy-(di-p-phenylen)-dimaleinimid, N,N'-Methylen-(di-p-phenylen)-dimaleinimid,
15 N,N'-Ethylen-(di-p-phenylen)-dimaleinimid, N,N'-Sulfo-(di-p-phenylen)-dimaleinimid, N,N'-m-Phenylen-bis-(p-oxyphenylen)-dimaleinimid, N,N'-Methylen-(di-1,4-cyklohexylen)-dimaleinimid, N,N'-Isopropyliden-(di-1,4-cyklohexen)-dimaleinimid, 2,5-Oxadiazolylen-dimaleinimid, N,N'-p-Phenylen-(dimethylen)-dimaleinimid, N,N'-2-Methyl-p-toluylen-dimaleinimid, N,N'-Hexamethylen-bis-(methylmaleinimid), N,N'-Thio-(diphenylen)-bis-(methylmaleinimid), N,N'-Methylen-(di-p-phenylen)-bis-(chlormaleinimid) oder N,N'-Hexamethylen-bis-(cyanmethylmaleinimid) ist.
20
9. Eine Zusammensetzung gemäß Anspruch 8, dadurch gekennzeichnet, daß das Imid 4,4'-bis-(Maleinimido)-diphenylmethan, ein Bispolymer von 1,4-Pyrrol-2,5-dion-1,1-(methylen-di-1,4-phenylen)-mit Methylen-bis-(benzamin) und 1,1-(Methylendi-4,1-phenylen)-bismaleinimid ist.
25
10. Eine Zusammensetzung gemäß jedem der Ansprüche 1 bis 9, worin die Imidkomponente im Bereich von 0,1-10% enthalten ist.
11. Eine Zusammensetzung gemäß Anspruch 10, dadurch gekennzeichnet, daß die Imidkomponente im Bereich von 1-5% enthalten ist.
30
12. Ein Verfahren zum Verkleben von zwei Substraten aus verschiedenen Materialien, dadurch gekennzeichnet, daß es das Auftragen einer Zusammensetzung gemäß Anspruch 1 zwischen die Substrate und das Aneinanderfügen der Substrate in einer fixierten Anordnung über eine Zeitdauer, die ausreicht,
35 um das Vernetzen der Zusammensetzung zu ermöglichen, umfaßt.
13. Ein Verfahren gemäß Anspruch 12, dadurch gekennzeichnet, daß das erste Substrat ein Polyalkylenterephthalat, eine Mischung Polyalkylenterephthalat/Polycarbonat oder Polyphenylensulfid und das zweite Substrat ein Metall mit einem hohen thermischen Ausdehnungskoeffizienten ist.
40
14. Ein Verfahren gemäß Anspruch 13, dadurch gekennzeichnet, daß das zweite Substrat Aluminium oder Kupfer ist.
15. Eine elektronische Komponente, die in ein Gehäuse aus Polybutylenterephthalat, aus einer Mischung Polybutylenterephthalat/Polycarbonat oder aus Polyphenylensulfid eingebettet ist, worin das Einbettungsmaterial eine vernetzte Zusammensetzung gemäß Anspruch 1 ist.
45

Revendications

- 50 1. Composition caractérisée en ce qu'elle comprend :
1) un composé ou mélange de composés ayant plusieurs groupe époxy par molécule ;
2) une polyoxyalcoylène amine durcissante pour l'époxy; et

3) un composé imide choisi parmi ceux qui ont les formules :



dans lesquelles R et R' représentent, respectivement, des groupes organiques monovalents et bivalents ayant 200 atomes de carbone ou moins.

2. Composition selon la revendication 1, caractérisée en ce que le composant époxy est un composé époxy cycloaliphatique, une novolaque époxydée, un caoutchouc époxydé ou une résine dérivée de l'épichlorhydrine et des phénols dihydriques.

3. Composition selon la revendication 1 ou 2, caractérisée en ce que le composant époxy est un éther diglycidique de bisphénol A.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce qu'elle comprend un composé éthyléniquement insaturé photodurcissable et un photoinitiateur.

5. Composition selon la revendication 4, caractérisée en ce que le composé éthyléniquement insaturé est un ester (méth)acrylique.

6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que la polyoxalcoylène amine est représentée par la structure :



dans laquelle Y est un hydrogène, un radical méthyle ou un radical éthyle, Z est un radical hydrocarboné ayant de 2 à 5 atomes de carbone, n vaut au moins un et r est un nombre supérieur ou égal à 2.

7. Composition selon la revendication 6, caractérisée en ce que r est supérieur à 2 et en ce que le poids moléculaire de la polyoxalcoylène amine est égal ou supérieur à 5000.
8. Composition selon l'une quelconque des revendications 1 à 7, caractérisée en ce que l'imide est le N,N'-éthylènedimaléimide, le N,N'-hexaméthylènedimaléimide, le N,N'-décaméthylènedimaléimide, le N,N'-dodécaméthylènedimaléimide, le N,N'-oxydipropylènedimaléimide, l'éthylènedioxy bis(N-propylmaléimide), le N,N'-métaphénylènedimaléimide, le N,N'-paraphénylènedimaléimide, le N,N'-oxy-(diparaphénylène)dimaléimide, le N,N'-méthylène(diparaphénylène)dimaléimide, le N,N'-éthylène-(diparaphénylène)dimaléimide, le N,N'-sulfo(diparaphénylène)-dimaléimide, le N,N'-métaphénylène-bis-(paraoxyphénylène)dimaléimide, le N,N'-méthylène(di-1,4-cyclohexylène)-dimaléimide, le N,N'-isopropylidène(di-1,4-cyclohexène)dimoléimide, le 2,5-oxadiazolylènedimaléimide, le N,N'-paraphénylène-(diméthylène)dimaléimide, le N,N'-méthylparatoluylène dimaléimide, le N,N'-hexaméthylènedicitraconimide, le N,N'-thio(diphénylène)dicitraconimide, le N,N'-méthylène(diparaphénylène)-bis-(chloromaléimide) ou le N,N'-hexaméthylène-bis(cyanométhylmaléimide).
9. Composition selon la revendication 8, caractérisée en ce que l'imide est la 4,4'-bismaléimidodiphénylméthane, le bis-polymère de 1,4-pyrrole-2,5-dione-1,1-(méthylènedi-1,4-phénylène) avec la méthylène bis(benzylamine) et le 1,1-(méthylènedi-4,1-phénylène)bismaléimide.
10. Composition selon l'une quelconque des revendications 1 à 9 dans laquelle le composant imide est présent dans un intervalle allant de 0,1 à 10%.
11. Composition selon la revendication 10, caractérisée en ce que le composant imide est présent dans un intervalle allant de 1 à 5%.
12. Procédé de liaison de deux substrats de matières différentes, caractérisé en ce qu'il comprend l'application d'une composition selon la revendication 1 entre les substrats et la réunion des substrats dans une relation de fixation pendant une durée suffisante pour permettre à la composition de se durcir.
13. Procédé selon la revendication 12, caractérisé en ce que le premier substrat est un téréphtalate de polyalcoylène, un mélange de téréphtalate de polyalcoylène et de polycarbonate ou un sulfure de polyphénylène et le second substrat est un métal ayant un coefficient de dilatation thermique élevé.
14. Procédé selon la revendication 13, caractérisé en ce que le second substrat est l'aluminium ou le cuivre.
15. Composant électronique enrobé dans un boîtier de téréphtalate de polybutylène, de mélange de téréphtalate de polybutylène et de polycarbonate ou de sulfure de polyphénylène, où la matière dans laquelle est enrobé le composant est une composition durcie selon la revendication 1.